

# The distribution of depleted uranium contamination in Colonie, NY, USA

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## Abstract

Uranium oxide particulates were dispersed into the environment from a factory in Colonie (NY, USA) by prevailing winds during the 1960's and '70's. Uranium concentration and isotope ratios from bulk soil samples have been accurately measured using inductively coupled plasma quadrupole mass spectrometry (ICP-QMS) without the need for analyte separation chemistry. The natural range of uranium concentrations in the Colonie soils has been estimated as  $0.7 - 2.1 \mu\text{g g}^{-1}$ , with a geometric mean of  $1 \mu\text{g g}^{-1}$ ; the contaminated soil samples comprise uranium up to  $500 \pm 40 \mu\text{g g}^{-1}$ . A plot of  $^{236}\text{U}/^{238}\text{U}$  against  $^{235}\text{U}/^{238}\text{U}$  isotopes ratios describes a mixing line between natural uranium and depleted uranium (DU) in bulk soil samples; scatter from this line can be accounted for by heterogeneity in the DU particulate. The end-member of DU compositions aggregated in these bulk samples comprises  $(2.05 \pm 0.06) \times 10^{-3} \text{ }^{235}\text{U}/^{238}\text{U}$ ,  $(3.2 \pm 0.1) \times 10^{-5} \text{ }^{236}\text{U}/^{238}\text{U}$ , and  $(7.1 \pm 0.3) \times 10^{-6} \text{ }^{234}\text{U}/^{238}\text{U}$ . The analytical method is sensitive to as little as  $50 \text{ ng g}^{-1}$  DU mixed with the natural uranium occurring in these soils. The contamination footprint has been mapped northward from site, and at least one third of the uranium in a soil sample from the surface 5 cm, collected 5.1 km NNW of the site, is DU. The distribution of contamination within the surface soil horizon follows a trend of exponential decrease with depth, which can be approximated by a simple diffusion model. Bioturbation by earthworms can account for dispersal of contaminant from the soil surface, in the form of primary uranium oxide particulates and uranyl species that are sorbed to organic matter. Considering this distribution, the total mass of uranium contamination emitted from the factory is estimated to be c. 4.8 tonnes.

## 1. Introduction

The by-product of uranium enrichment, where the fissile isotope  $^{235}\text{U}$  is artificially concentrated for use as nuclear fuel or weapons, is depleted uranium (DU). In contrast to natural uranium, DU typically comprises  $(2 - 3) \times 10^{-3} \text{ }^{235}\text{U}/^{238}\text{U}$ , is also depleted in  $^{234}\text{U}$ , and is contaminated by anthropogenic  $^{236}\text{U}$  from reprocessed uranium (Bleise et al. 2003). Worldwide nuclear programmes have amassed c. 1.2 million tonnes of DU, most of which is stored as  $\text{UF}_6$  (NEA & IAEA 2001). Applications for depleted uranium metal include ballast, munitions and radiation shielding. The use of armour piercing DU munitions (kinetic energy penetrators) in the Gulf and Balkans conflicts, and recently the Iraq invasion has been highly controversial, because they disperse a radioactive and toxic material into the environment. However, DU exposure is unlikely to present a significant health risk (e.g. Priest 2001).

The Royal Society (2001; 2002) reports focus on the health risks from inhalation of DU particulates. The reports recommended that the environmental behaviour of alloys and particles of DU,

should be compared to natural uranium minerals, and information should be obtained on their bioavailability.

Several recent studies have investigated the environmental behaviour of DU metals, which corrode in oxidising environments to form soluble uranyl species (e.g. Buck *et al.* 2004; Schimmack *et al.* 2005; Fomina *et al.* 2008; Handley-Sidhu *et al.* 2009). The DU particulates released from munitions impacting armour are characterised in Krupka *et al.* (2009) and other papers in *Health Physics* **96** (3) resulting from the Capstone Aerosols study (Parkhurst *et al.* 2004). These and the particulates from the combustion of DU metals are introduced to the environment in a range of oxidation states:  $\text{UO}_2 - \text{UO}_{2+x} - \text{U}_3\text{O}_8 - \text{UO}_3$ .  $\text{UO}_3$  and uranyl species are thermodynamically favoured, but bulk oxidation to these more soluble oxides is limited by slow kinetics and surface passivation (McEachern & Taylor 1998). This appears to be the case for the persistence of low solubility  $\text{UO}_{2+x}$  (hyperstoichiometric  $\text{UO}_2$ ) and  $\text{U}_3\text{O}_8$  particles in soils (Chapter 3 / Lloyd *et al.* 2009b). Radiogenic lead reduces the mobility of uranium from natural uraninite (e.g. Finch & Ewing 1992), which otherwise is a logical analogue. Studies by Oliver *et al.* (e.g. 2008) have recently made environmental observations on the distribution of contamination from DU munitions test firing. A number of other studies have characterised individual particles from environmental samples contaminated by the combustion of uranium metals and DU munitions (e.g. Török *et al.* 2004; Salbu *et al.* 2005; Lind *et al.* 2009).

This aim of this environmental case-study is to identify the processes that affect the distribution and bioavailability of uranium from DU particulate contamination. The field site offers an accessible and large contamination footprint, with the absence of confounding contamination from DU metal fragments, and more than 25 years of environmental processing. It is therefore an attractive analogue for battlefield contamination, and potentially for epidemiological studies related to DU particulate inhalation exposure.

Natural uranium comprises three isotopes:  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{234}\text{U}$ , all of which are unstable with long half-lives. The 'convention' value for  $^{235}\text{U}/^{238}\text{U}$  (atom ratio,  $n^{235}\text{U}/n^{238}\text{U}$ ) is  $7.253 \times 10^{-3}$  (Steiger & Jäger 1977), recently recommended as  $7.257 \times 10^{-3}$  (De Laeter *et al.* 2003), with slight (‰) natural fractionation about this value (Weyer *et al.* 2008). Except for the Oklo natural reactors (Neuilly *et al.* 1972) deviation of  $^{235}\text{U}/^{238}\text{U}$  implies anthropogenic contamination. Uranium in secular equilibrium has a  $^{234}\text{U}/^{238}\text{U}$  ratio of  $5.5 \times 10^{-5}$  (Richter *et al.* 1999), but there are significant natural deviations from this ratio (e.g. Fleischer 2008). The abundance of  $^{236}\text{U}$  in natural uranium is negligible (e.g. Berkovits *et al.* 2000).

The distribution of uranium within the Earth is discussed in Plant and Saunders (1996), the continental crust comprises an average  $2.7 \mu\text{g g}^{-1}$  (Taylor 1964), hosted in resistate igneous accessory minerals including thorite, monzanite and zircon, and occasionally concentrated in ore minerals including uraninite and pitchblende (impure uranium oxides), and coffinite (a hydrated uranium silicate). The natural background concentration is variable in environmental samples, typically low  $\mu\text{g g}^{-1}$  and  $\text{ng g}^{-1}$  levels.

As discussed previously, natural environmental samples comprise variable trace quantities of uranium, but anthropogenic contamination can be determined from  $^{235}\text{U}/^{238}\text{U}$ . Analytical methods for determining uranium in environmental samples were reviewed in Wolf (1999), the precision of radiometric techniques is often limited by the low activities of the uranium isotopes. Mass spectrometry techniques can achieve good precision, especially for isotope ratios. Isotope dilution thermal ionisation mass spectrometry (ID-TIMS) offers the best precision, but is costly and requires

laborious sample preparation. Taylor *et al.* (1998) obtained relative uncertainties of 0.2 % ( $k = 2$ ) for  $^{235}\text{U}/^{238}\text{U}$  from soil samples using single-spike ID-TIMS.

The performance of four inductively coupled plasma mass spectrometers (ICP-MS, multi and single collector sector field, and quadrupole) in combinations with several nebulisers (ultrasonic and desolvating), measuring  $^{236}\text{U}/^{238}\text{U}$ , are compared in Boulyga *et al.* (2002). The multicollector ICP-MS (MC-ICP-MS) achieved excellent precision; and the desolvating nebuliser reduced hydride interference by up to two orders of magnitude. Quadrupole ICP-MS (ICP-QMS) instruments offer lower costs with generally good precision. As for most ICP techniques, sample dissolution is required. Analyte separation chemistry is often preferred (e.g. Zheng & Yamada 2006), but it is desirable to avoid this costly step. Other than hydride, there appears to be little potential for polyatomic interferences on the uranium isotopes (Lariviere *et al.* 2006). Ehrlich *et al.* (2004) found analyte separation to be unnecessary for  $^{234}\text{U}/^{238}\text{U}$  measurements from manganese nodules, although deposition of dissolved solids on the sampler and skimmer cones could be an issue. However, Gwiazda *et al.* (2004) and Shen *et al.* (2002) experienced background interferences on  $m/z$  235 when working at very low uranium concentrations; the latter study attributed this to organic rich samples and the interference was removed by separation chemistry.

A significant objective of this case-study is to define the present distribution of DU contamination. ICP-QMS was used for the determination of uranium isotope ratios from trace concentrations in contaminated soil samples. Adequate precision was realised using a desolvating nebuliser, and without the need for analyte separation chemistry. There is heterogeneity in the isotopic composition of DU contaminant (Chapter 5 / Lloyd *et al.* 2009c) and the effect of this variability on the isotopic compositions of bulk environmental samples is explored in this paper. The dataset demonstrates the clarity for resolving DU contamination that precise  $^{235}\text{U}/^{238}\text{U}$  ratios coupled with high productivity offer.

## 2. The Colonie case-study

### 2.1. Site history

National Lead Industries (NLI) operated a factory in Colonie (NY, USA), from 1958 – 1984. The factory reduced  $\text{UF}_4$  to metal, and machined depleted uranium articles including kinetic energy penetrators, counterweights and radiation shielding (ATSDR 2004). The storage of scrap uranium metal is hazardous, because this material is pyrophoric when it is finely divided. Therefore, this waste was converted to uranium oxides in a furnace, which resulted in emissions of uranium oxide aerosols to the atmosphere. This was not contemporary best practice (Wilkinson 1962). National Lead were also responsible for uranium contamination surrounding the Fernald site in Ohio (Buck *et al.* 1996).

The history of permits for the NLI site is documented in a draft report by the New York State Department of Health (1979). In 1968, it was noted that the converter stack operated without filtration, and immediately south of the site  $^{238}\text{U}$  soil concentrations of  $163 \mu\text{g g}^{-1}$  were reported; Department of Labour permitted nearly  $600 \mu\text{g g}^{-1}$  on site at that time. In 1973 NLI were permitted to discharge a total of 3.9 kg of uranium from 23 stacks. In 1975 the site was limited to handling natural and depleted uranium, but prior to this licences were also held for enriched uranium and thorium. In 1977, when production increased, an electrostatic precipitator was added to the conversion furnace (chip-burner), although this was reportedly bypassed (NYSDOH 1979; Romano 1982).

In May 1979 routine analysis of air filters, sampled at locations 40.8 and 15.7 km NNW of the NLI site, revealed contamination by micrometer diameter DU particles (Dietz 1980). A survey

conducted later that year revealed extensive depleted uranium contamination of soils surrounding the site (Jeter & Eagleson 1980). The legal proceedings that led to the closure of NLI for excessive emissions of uranium to the environment are detailed in Romano (1982).

In 1984, US Department of Energy took over responsibility for the site, and since 1997 the U.S. Army Corps of Engineers has been responsible for the environmental remediation of the site under the Formerly Utilized Site Remedial Action Program (USACE 2009). The remediation threshold used for soils is 35 pCi g<sup>-1</sup> from <sup>238</sup>U (USACE 2002), equivalent to 104 µg g<sup>-1</sup>, highly conservative when compared to 190 pCi g<sup>-1</sup> derived by Dunning (1996). Remediation of the site and limited remediation of surrounding properties, involving removal and disposal of contaminated soils, is reported to have cost US\$ 190 million (Dlouhy 2009).

Contamination is evident in reservoir sediments at a site downstream of NLI (Arnason & Fletcher 2003; Lo *et al.* 2006; Arnason *et al.* 2008). Depleted uranium has been detected in the urine of former employees (with enriched uranium from one individual) and from some residents (Parrish *et al.* 2008).

Examination of contaminated soils and dusts reveals primary uranium oxide particles in the size range 0.5 – 150 µm, including mixed UO<sub>2+x</sub> and U<sub>3</sub>O<sub>8</sub> spheres with diameters 20 – 64 µm, and rarely secondary uranium precipitates (Chapter 3 / Lloyd *et al.* 2009b). These spheres and other specific particle morphologies are directly comparable to those from munitions. Laser ablation (LA-) MC-ICP-MS reveals a spread of depleted uranium isotope ratios from individual particles, attributed to variations in the NLI feedstocks (Chapter 5 / Lloyd *et al.* 2009c).

## 2.2. Environmental setting

The NLI site is located between Colonie and Albany, NY, USA (Figure 1). The NLI site neighbours other industrial sites, and is close to two busy roads and a railway, the surrounding area (within 3 km) is mainly suburban with gentle topography. Construction of highway I90, State University of New York (SUNY) Albany campus, and the Harriman Campus during the 1960s relandscaped much of the area within a 2 km quadrant SW of NLI.

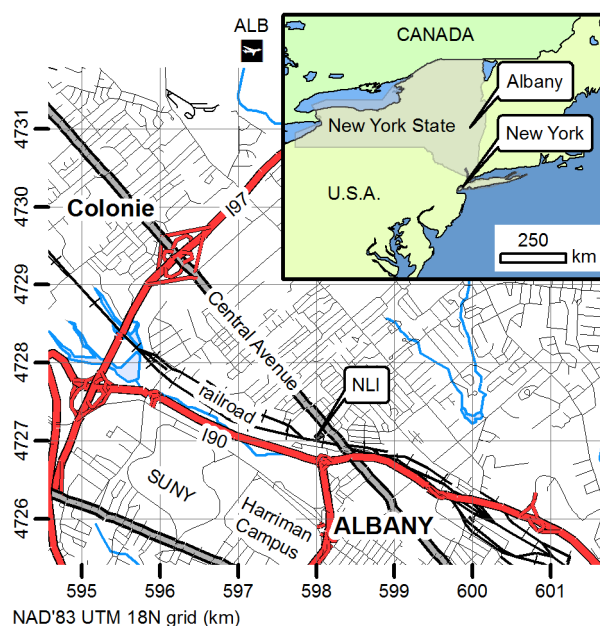


Figure 1. Location map for the NLI site, which is located between Colonie and Albany, NY, USA. Base map with permission (US Department of Commerce 2001).

The soils within 3 km of NLI are dominated by generally well-drained loamy fine sands; with little pedogenic horizon development, less than 14 wt. % clay, acid pH and negligible carbonate content (USDA 2006). The soil samples collected for this study had a pH range of 3.2 – 7.6, median 5.3 ( $n = 208$ ). There is typically a thin, < 1 cm, leaf litter layer covering a 15 – 25 cm thick organic-rich mineral-sand horizon (A). These soils are derived from aeolian dune deposits (well sorted silica rich fine-sands), kame deposits, lacustrine sands and some clays, which overlie the Normanskill Shale of the Middle Ordovician (NYS Geological Survey 1999). The Colonie soils contain small quantities of detrital zircons, which host natural uranium.

The mean uranium concentration of 19 sediment samples from within 12 km of NLI, analysed by X-ray fluorescence for the NURE programme (USGS 2004), was  $0.6 \mu\text{g g}^{-1}$ . Uranium air concentrations for air samples collected in Albany in 1969 were c.  $0.5 \text{ ng m}^{-3}$ , or  $5 \mu\text{g g}^{-1}$  of total suspended particulate (concentrated relative to sediments), within the range of those reported from elsewhere in New York State (McEachern *et al.* 1971).

Vegetation in the area includes deciduous and coniferous woodlands, and the native Albany Pine Bush ecosystem including pitch pine (Albany Pine Bush Preserve Commission 2005). The Köppen-Geiger climate zone is Dfa, “cold, without dry season, hot summer” (Peel *et al.* 2007).

In addition to depleted uranium, the NLI site has also handled other hazardous materials including enriched uranium, thorium, heavy metals (including Pb, Ni, Sb and Cd) and polychlorinated biphenyl (PCB) oils. Some of these materials were dumped into a lake that adjoined the NLI site (ATSDR 2004). A ‘US Superfund’ site, remediated for mercury and PCB oil contamination is located approximately 900 m WNW of NLI (EPA 1983). The Patroon creek, which runs parallel to highway I90 and into which NLI discharged waste water via a culvert, was previously classified as one of the ten most severely polluted streams in New York State (refs. in Arnason & Fletcher 2003).

### 2.3. Background data

In 1979 NLI were required to commission a survey of soils surrounding the Colonie site. Surface soil samples (0 - 1.3 and 1.3 - 5.1 cm) from within 600 m of NLI were analysed by gamma-ray spectrometry and reported in Jeter and Eagleson (1980). The gamma-ray spectrometry data have poor precisions, typically  $\pm 32\%$  for  $^{235}\text{U}/^{234}\text{Th} \approx ^{235}\text{U}/^{238}\text{U}$ . The  $^{234}\text{Th}$  activity data ( $\pm 14\%$ ) have been converted to uranium concentrations, which have been interpolated by ordinary kriging using *ESRI Geostatistical Analyst* (Johnston *et al.* 2001), and are presented in Figure 2.

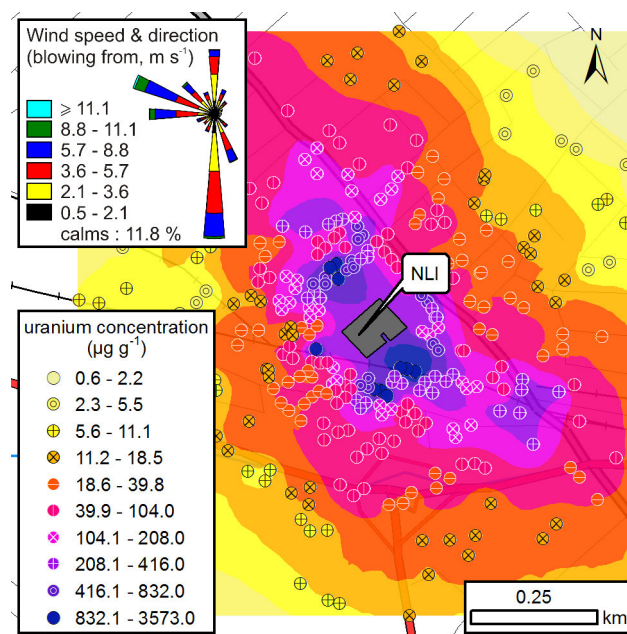


Figure 2. Ordinary kriging of 1979 soil survey data (log-transform, quadratic trend removal, exponential semivariogram model; cross validation statistics: mean standardised error 0.004; RM<sup>2</sup> standardised error 0.98). The distribution of uranium was clearly controlled by the prevailing winds. From this interpolated dataset, it is estimated that c. 3.2 tonnes of uranium contaminated the surface 5.1 cm of soils within 600 m of NLI. Wind rose from Albany County Airport data, 1961 - 1979 (WebMet.com 2002; Lakes 2005).

The areal distribution of uranium surrounding NLI was clearly controlled by the prevailing winds; and can be attributed to aerial deposition of uranium particulate emissions. The total mass of contaminant uranium in the surface soils, to a depth of 5.1 cm and a distance of 600 m from NLI, is estimated in the order of 3.2 tonnes<sup>1</sup> (from the integration of the interpolated dataset, with an estimated  $0.8 \pm 0.1 \text{ g cm}^{-3}$  dry unconsolidated soil density, and a mean natural background of  $1 \text{ µg g}^{-1}$  uranium). The natural background is determined in Section 5.2, and the mass beneath 5.1 cm is estimated in Section 5.3.

To place this in context, the natural uranium in this volume of soil is approximately 54 kg. The Colonie contamination is significant compared to 321 tonnes DU deployed during the Gulf War (Bleise *et al.* 2003) of which a small fraction was aerosolised and spread over numerous locations.

<sup>1</sup> It is difficult to calculate the uncertainty involved in this figure; it was estimated to be in the order of  $\pm 0.5$  tonnes.

These quantities are small compared to the emissions of heavy metals from large smelters, e.g. Rawlins *et al.* (2006) estimated that 2500 tonnes of lead particulates contaminated Humberside (UK).

The NLI contamination footprint equates to an average  $2 \text{ g m}^{-2}$  deposition over the 1979 survey area, but is substantially concentrated towards the site. Approximately 49 % was deposited within 200 m of NLI, and 80 % within 400 m. Our previous estimate of 5 tonnes incorrectly assumed a higher soil density (Parrish *et al.* 2008). It is apparent that annual discharges of 3.9 kg permitted in 1973 were not typical of the plant's history, averaging 139 kg per annum from 1958 – 1981.

### 3. Methodology

#### 3.1. Sampling

Soil sampling was conducted during 2006 and 2007. Due to the limited number of easily accessible and apparently undisturbed sampling locations, it was not possible to follow a designed sampling strategy for this study, i.e. sampling had to be more ad hoc. Most of the sampling locations in this suburban environment were in wooded areas, scrubland and on public land. A number of areas are either less accessible, or they have been substantially re-landscaped during the 1960s, e.g. Albany International Airport, the Harriman Campus, University at Albany (SUNY), I90, and the more densely populated neighbourhood south of I90 (see Figure 1).

Soil samples were collected using a cleaned hand-auger, after removal of vegetation and leaf litter from the soil surface. The top 5 cm was bagged separately to the remaining 5 – 15 cm sample. Thus, the samples are mainly organic rich loamy fine sands (A horizon). For each location, a sample was collected from five points over a ten-metre square, totalling approximately 0.5 kg soil. Sampling duplicates were taken from approximately one in ten locations, from an offset square. Soil profiles were sampled by digging a pit and collecting from a cleaned surface.

#### 3.2. Sample preparation and dissolution

Soils samples were dried at 40 – 60 °C for 24 - 72 hours, sieved to less than 2 mm, and split into two subsamples. A 60 g aliquot from each sample was ground to a fine powder in an agate ball mill (aiming for < 63 µm grain size).

The aim of the sample digestion methodology (after Green 2007) is for total dissolution. For each digestion, one gram of the powdered soil was weighed into an acid-leached PFA vessel (Saville), 20 ml of concentrated HNO<sub>3</sub> was added, the vessel sealed and refluxed at 120 °C for 8 hours, then opened and evaporated. 8 ml of HNO<sub>3</sub>, 4 ml HClO<sub>4</sub> and 10 ml HF were added to each vessel, which was heated to 80 °C for 8 hours, before being evaporated to near-dryness at 160 °C. The contents were dissolved in 10 ml 50 % HNO<sub>3</sub> and 10 ml H<sub>2</sub>O<sub>2</sub>, and then diluted to 100 ml (i.e. 1 % soil in a 5 % HNO<sub>3</sub> matrix). Prior to analysis, the solutions were diluted to 0.1 % or less in 1 % HNO<sub>3</sub>. Typical digestion blank levels are c. 4 ng uranium (using BDH Aristar analytical grade reagents and MilliQ 18 MΩ deionised water).

Prior to MC-ICP-MS analysis, uranium was separated from a sub-set of the soil solutions. The solutions were adjusted to 4M HNO<sub>3</sub> (double quartz distilled), and then pipetted onto pre-leached dipentyl pentylphosphonate (Eichrom Industries UTEVA<sup>®</sup>, described Horwitz *et al.* 1992). The uranium was then eluted using 0.6 M HCl, this solution was evaporated to dryness, H<sub>2</sub>O<sub>2</sub> was added and then evaporated, and finally dissolved in 1 ml 2% HNO<sub>3</sub>. Typical laboratory blanks for the separation chemistry in the class 100 clean room are < 100 fg uranium.

### 3.3. Analytical

The diluted sample digests were analysed at the British Geological Survey (Keyworth, UK) using ICP-QMS (VG Elemental Excell). Concentrations were determined in a separate run to the isotope ratios, using external multi-element standards (2, 5, 10 ng ml<sup>-1</sup> concentration) and an internal Re monitor solution added by T-piece prior to nebulisation (concentric flow, 1 ml min<sup>-1</sup>).

For isotope ratio analysis, the sample digests were diluted to achieve 0.6 - 1 million counts per second from <sup>238</sup>U on the ion counter (typically from 1 – 4 ng ml<sup>-1</sup> at 0.1 ml min<sup>-1</sup>). A desolvating nebuliser (Cetac Technologies Aridus II) was used for isotope ratio runs, to minimise hydride interference and maximise sensitivity. Analytical runs were limited to about 60 sample solutions due to fouling of the Ni sampler and skimmer cones, which significantly reduced sensitivity. However, these can be cleaned for less cost than analyte separation chemistry.

Natural uranium solutions were used as external standards (US Geological Survey SDO-1 or Institute for Reference Materials and Measurements REIMEP 18-A). The instrument was operated in peak jumping mode, acquiring 15 measures integrated from 920 sweeps across *m/z* 233, 234, 235, 236 & 238, with dwell times of 5 milliseconds. Blank, hydride and mass-bias corrections were applied to the data. In actuality the hydride correction from *m/z* 236 / *m/z* 235, typically c. 10<sup>-5</sup>, is convolved with abundance sensitivity from <sup>238</sup>U peak tails (not measured), but is not significant to the reported data. The mass bias, typically c. 0.3 % for <sup>235</sup>U/<sup>238</sup>U and assumed linear with mass, is the significant correction. Uncertainty (*k* = 2) was propagated from the instrumental standard error of the mean (*n* = 15) and the relative standard deviations of the corrected QC solutions.

A subset of the soil samples were analysed at the NERC Isotope Geosciences Laboratory (Keyworth, UK) using MC-ICP-MS (VG Elemental Axiom) with a desolvating nebuliser (Cetac Technologies Aridus), after separation of the analyte uranium from its matrix. Abundance sensitivity, hydride, and mass-bias were corrected for using an external standard (U950A, natural uranium solution, assuming the convention value <sup>235</sup>U/<sup>238</sup>U 7.253 x 10<sup>-3</sup>).

Total carbon was measured in triplicate from infrared absorption by combustion gases (LECO CS230, Stockport, UK). Soil pH was measured from unmilled soils using a calibrated Pt electrode in a 1 g : 2.5 ml 0.01 M CaCl<sub>2(aq)</sub> slurry.

Ordinary kriging was used to interpolate the sample data using *ESRI Geostatistical Analyst* (Johnston *et al.* 2001). A log transform was used for heavily skewed datasets, and a quadratic function for trend removal. The cross-validation error statistics were optimised by changing the semivariogram model, lag size, and ‘neighbours included’ parameters. Exponential semivariogram models and 8 sector ‘neighbourhood searches’ were appropriate because it was apparent from the data that contamination falls off exponentially and is directional (see Section 5.5). Reasonable cross-validation error statistics were achieved, and these are summarized with the methodology in the figure captions.

## 4. Quality Control

### 4.1. Uranium concentrations

The ICP-QMS concentration data for three quality control (QC) solutions are presented in Table 1. Reference materials SDO-1 (U.S. Geological Survey, shale powder, c. 9.7 % organic carbon) and JR-2 (Geological Survey of Japan, rhyolite powder) were included in each digestion batch to monitor dissolution and analyte recovery. There is a slight, but minimal, positive bias for the independent multi-element standard. SDO-1 was underestimated by c. 4 %; JR-2 was within the expected range.



QC solution	n	uranium concentration ( $\mu\text{g g}^{-1}$ or $\text{ng ml}^{-1}$ )
QC-A** target value	53	$10.14 \pm 0.08$ 10
SDO-1 reference value **	9	$46 \pm 1$ 47.9 - 48
JR-2 reference value**	12	$11.7 \pm 0.3$ 10.2 - 12.0

**Table 1.** Quality control data for the measured QC solutions. \* QC-A is an independently prepared multi-element standard solution with a target concentration of  $10 \text{ ng ml}^{-1}$ ; \*\* GeoReM recommended values (Jochum *et al.* 2005). Uncertainty from standard error of the mean ( $k = 2$ ).

A Thompson-Howarth duplicate control chart (Thompson & Howarth 1978; amc 2002b) for the uranium concentration data is presented in Figure 3. The estimated analytical uncertainty is  $\pm 8.8 \%$  ( $k = 2$ ).

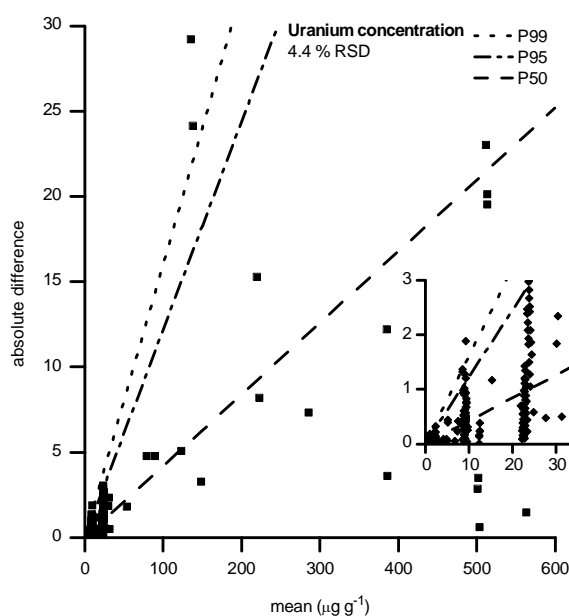


Figure 3. Thompson-Howarth duplicate control chart (Thompson & Howarth 1978; amc 2002b) for uranium concentrations measured by ICP-QMS, which was used to estimate an RSD of 4.4 % ( $k = 1$ ,  $n = 189$ ).

#### 4.2. Uranium isotope ratios

The MSWD (Wendt & Carl 1991) of the  $^{236}\text{U}/^{238}\text{U}$  data from REIMEP 18-C suggested that the propagated uncertainties were underestimated, so these were expanded by 5 %. The lower limit of detection (LLD) for  $^{236}\text{U}/^{238}\text{U}$  by ICP-QMS was estimated as  $2 \times 10^{-6}$ .

Thompson-Howarth duplicate quality control charts, suggested that  $^{235}\text{U}/^{238}\text{U}$  uncertainty was underestimated using instrumental standard error; standard deviation appears more appropriate. This is possibly because for  $^{236}\text{U}$  and  $^{234}\text{U}$ , precision is limited by counting statistics, but plasma noise may be significant for  $^{235}\text{U}$ .

Thompson-Howarth duplicate quality control charts for the isotope ratio analyses are presented in Figure 4. These confirm that the expanded uncertainties are appropriate for the sample data. The typical relative uncertainty ( $k = 2$ ) of 1.8 % for  $^{235}\text{U}/^{238}\text{U}$  is adequate for this application.

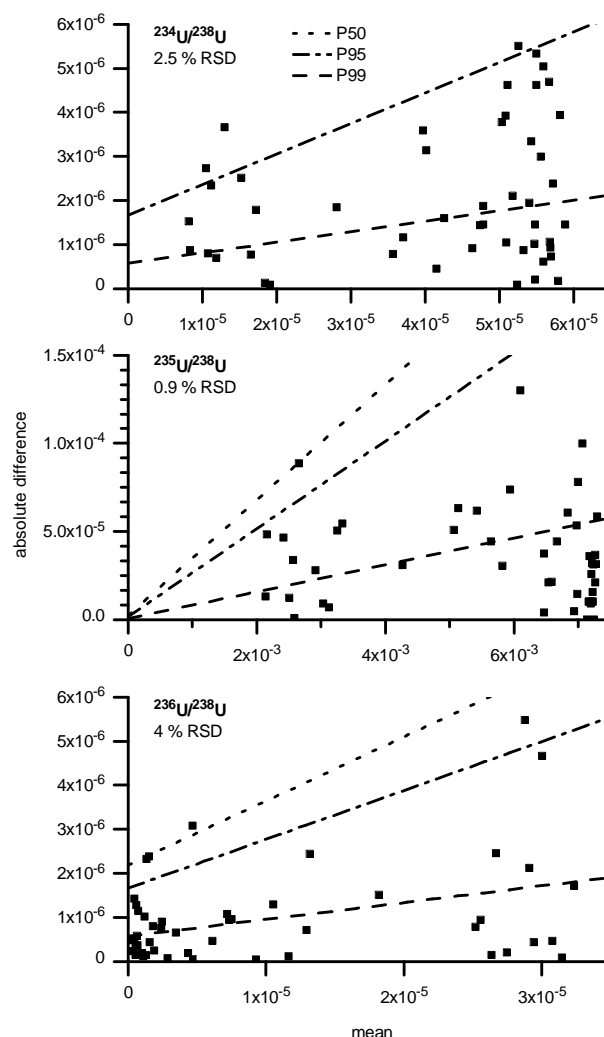


Figure 4. Thompson-Howarth duplicate control chart (amc 2002b) for uranium isotope ratios measured by ICP-QMS, used to assess analytical uncertainty ( $k=1$ ,  $n = 49$ ).

Table 2 summarises the results of multiple analyses of quality control solutions. Two are reported (marginally) outside of the reference values; these are for highly enriched uranium, exaggerating minor inaccuracy in the mass bias correction or detector linearity. The quality control solutions available for  $^{236}\text{U}/^{238}\text{U}$  are not ideal for DU due to the relatively high abundance of  $^{236}\text{U}$  and  $^{235}\text{U}$ .

QC Solution	n	$^{234}\text{U}/^{238}\text{U} (\times 10^{-5})$	$^{235}\text{U}/^{238}\text{U} (\times 10^{-3})$	$^{236}\text{U}/^{238}\text{U} (\times 10^{-5})$
REIMEP 18-A reference value*	29	$5.66 \pm 0.05$ $5.6582 \pm 0.0041$	$7.257 \pm 0.008$ $7.2542 \pm 0.0036$	$< 0.2$ $0.0030579 \pm 0.0000083$
REIMEP 18-B reference value*	7	$33.1 \pm 0.5$ $33.271 \pm 0.022$	$35.3 \pm 0.1$ $35.470 \pm 0.018$	$38.5 \pm 0.8$ $38.828 \pm 0.013$
REIMEP 18-C reference value*	38	$7.90 \pm 0.05$ $7.9510 \pm 0.0068$	$4.385 \pm 0.006$ $4.3794 \pm 0.0027$	$102.9 \pm 0.9$ $103.370 \pm 0.044$
REIMEP 18-D reference value*	7	$21.0 \pm 0.3$ $20.936 \pm 0.014$	$24.11 \pm 0.08$ $24.233 \pm 0.012$	$< 0.2$ $0.011054 \pm 0.000029$
JR-2 (natural) reference value	28	$5.48 \pm 0.05$ $5.486 - 5.49^{**}$	$7.26 \pm 0.01$ $7.257 \pm 0.009$	$< 0.2$ $< 0.00001$
SDO-1 (natural) reference value	25	$5.49 \pm 0.05$ <i>presumed c. 5.5</i>	$7.26 \pm 0.01$ $7.257 \pm 0.009$	$< 0.2$ $< 0.00001$
'NSLDU'***	11	$3.98 \pm 0.06$	$5.53 \pm 0.01$	$1.03 \pm 0.04$
MC-ICP-MS data	1	$3.9 \pm 0.1$	$5.54 \pm 0.02$	$0.9 \pm 0.1$

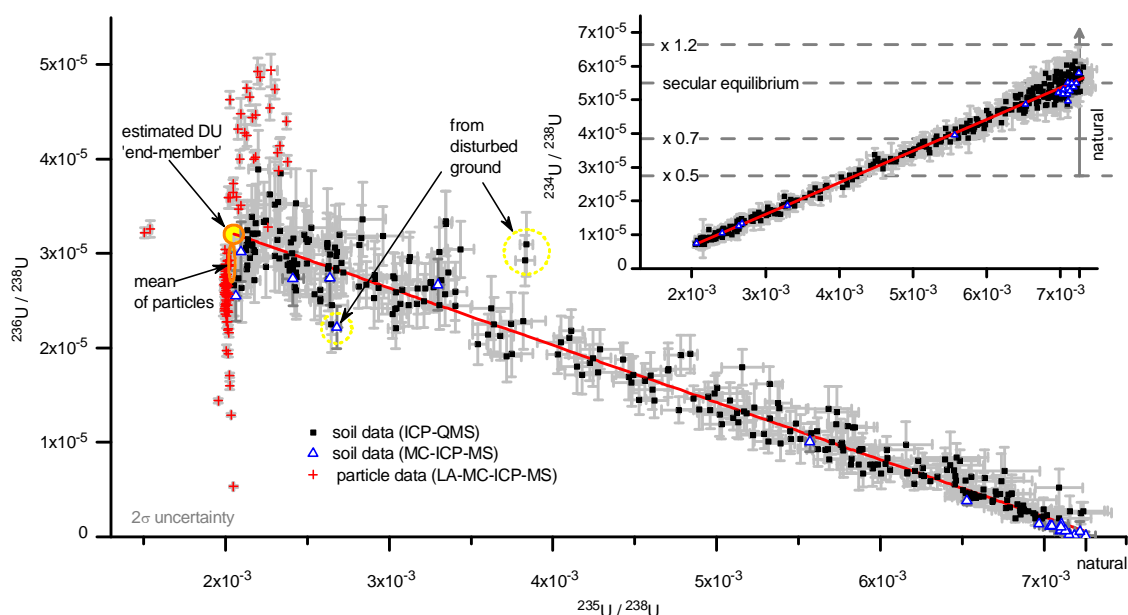
Table 2. Quality control data for 5 reference solutions, data reported as mean and standard error of the mean ( $k = 2$ ). The majority of the data are within uncertainty of reference values. \* Richter *et al.* (2006); \*\* GeoReM recommended value (Jochum *et al.* 2005); \*\*\* monitor solution from Colonie soil digest, compared with MC-ICP-MS analysis.

Twenty soil digests from across the isotope ratio range, were analysed by MC-ICP-MS (after uranium separation chemistry) for comparison with the ICP-QMS data. For  $^{235}\text{U}/^{238}\text{U}$ , all of the ICP-QMS ratios were well within uncertainty of the MC-ICP-MS. MC-ICP-MS achieving c. 2.5 times higher measurement precision cf. ICP-QMS. For  $^{234}\text{U}/^{238}\text{U}$ , one in twenty was outside of uncertainty (appropriate for 95 % confidence interval), also without systematic bias. Of the seven  $^{236}\text{U}/^{238}\text{U}$  ratios quantified by ICP-QMS, there was a slight positive bias relative to the MC-ICP-MS data, but all were reported within uncertainty.

Slightly higher  $^{235}\text{U}/^{238}\text{U}$  precision (1 %) was reported by Zheng and Yamada (2006) after analyte separation chemistry.  $^{232}\text{Th}^1\text{H}_2$  interference on  $^{234}\text{U}/^{238}\text{U}$  is highly unlikely to be an issue as  $^{235}\text{U}^1\text{H}$  was minimised by the desolvating nebuliser. There is no evidence of positive bias in  $^{235}\text{U}/^{238}\text{U}$  from the organic rich SDO-1, or for unseparated solutions when compared to analyte-separated solutions.

## 5. Results & Discussion

### 5.1. Isotope mixing Lines



**Figure 5.** Plot of  $^{236}\text{U}/^{238}\text{U}$  against  $^{235}\text{U}/^{238}\text{U}$ , defining a mixing line between NU and a DU end-member (weighted, adj.  $R^2$  0.97). At least some of the scatter can be accounted for by the heterogeneity of the particulate (data plotted from Chapter 5 / Lloyd *et al.* 2009c). The ‘average end-member’ DU composition is estimated  $(2.05 \pm 0.06) \times 10^{-3} \text{ }^{235}\text{U}/^{238}\text{U}$ ,  $(3.2 \pm 0.1) \times 10^{-5} \text{ }^{236}\text{U}/^{238}\text{U}$  ( $n = 405$ ). The ICP-QMS data are in agreement with the MC-ICP-MS. Two samples are highlighted as examples of scatter from the mixing line, which are discussed further in the text.

**Figure 5 Inset.** Plot of  $^{234}\text{U}/^{238}\text{U}$  against  $^{235}\text{U}/^{238}\text{U}$ ; there is less scatter on this mixing line (weighted, adj.  $R^2$  0.99). DU end-member estimated as  $(7.1 \pm 0.3) \times 10^{-6} \text{ }^{234}\text{U}/^{238}\text{U}$ ; NU  $(5.60 \pm 0.06) \times 10^{-5}$ . Lines mark secular equilibrium, the typical range of natural fractionation in soils, 0.7 – 1.2 (Szabo & Rosholt 1982), and 0.5 recorded for a natural geological sample (Fleischer 2008).

Figure 5 shows mixing lines between an average DU composition and natural uranium, there is no evidence for mixing with enriched uranium (which was also handled by NLI). The isotopic compositions of the particulate contamination are heterogeneous, which is reflected in the scatter of the bulk sample data from the mixing line (supported by MC-ICP-MS analyses).

The upper highlighted (duplicate) sample data deviate significantly from the line, requiring a high degree of ‘selectivity’ from the high  $^{236}\text{U}$  particle population. It is unlikely that this is from nugget effect. The location is on a small terrace of the stream that flows from the NLI site, and adjacent to an old rubbish tip on land cleared during the 1960’s. It is possible that related ground disturbance have masked earlier contamination, or that NLI liquid discharges were isotopically

distinct. The lower  $^{236}\text{U}$  data highlighted is also from disturbed ground, a filled depression that may have received NLI wastes.

The lowest measured  $^{235}\text{U}/^{238}\text{U}$  ratio from a bulk sample was  $(2.06 \pm 0.02) \times 10^{-3}$ , with a uranium concentration of  $220 \pm 19 \mu\text{g g}^{-1}$ . From this concentration, the sample probably comprises greater than 99 % DU of total uranium. The DU ‘end-member’ cannot be known precisely, and the particle data from Lloyd *et al.* (Chapter 5 / 2009c) show there were a variety of DU isotopic compositions used at NLI. The mean isotopic compositions of the particle data are  $(2.04 \pm 0.02) \times 10^{-3}$  for  $^{235}\text{U}/^{238}\text{U}$ , and  $(2.9 \pm 0.2) \times 10^{-5}$  for  $^{236}\text{U}/^{238}\text{U}$ , but these data may not be fully representative. For a  $^{235}\text{U}/^{238}\text{U}$  ratio of c.  $(2.05 \pm 0.06) \times 10^{-3}$ , from a linear functional relationship of maximum likelihood (amc 2002a), the  $^{236}\text{U}/^{238}\text{U}$  ratio is  $(3.2 \pm 0.1) \times 10^{-5}$ . The ‘average end-member’ is similar to the mean of the particle data.

The inset graph of  $^{234}\text{U}/^{238}\text{U}$  against  $^{235}\text{U}/^{238}\text{U}$  shows a well-defined mixing line between natural uranium and a depleted uranium end-member. There is less deviation from this mixing line, compared to  $^{236}\text{U}/^{238}\text{U}$  against  $^{235}\text{U}/^{238}\text{U}$ .  $^{234}\text{U}/^{238}\text{U}$  depletion is approximately equal to  $^{235}\text{U}/^{238}\text{U}$  depletion in an enrichment cascade, whereas  $^{236}\text{U}$  is from the introduction of variable quantities of reprocessed reactor tails to the cascade (Smith 1984). The estimated end-members comprise  $(5.60 \pm 0.05) \times 10^{-5}$   $^{234}\text{U}/^{238}\text{U}$  for natural uranium and  $(7.1 \pm 0.3) \times 10^{-6}$  for depleted uranium. Eighteen uranium oxide particles from Colonie have been individually analysed by MC-ICP-MS, with a mean  $^{234}\text{U}/^{238}\text{U}$  ratio of  $(7.3 \pm 0.1) \times 10^{-6}$ , which is in close agreement with the present estimate (Chapter 6 / Lloyd *et al. unpublished*).

There is some evidence of increased scatter with respect to  $^{234}\text{U}/^{238}\text{U}$  at the natural uranium end, c.  $\pm 0.3 \times 10^{-5}$ . The secular equilibrium of  $^{234}\text{U}/^{238}\text{U}$  is  $(5.50 \pm 0.02) \times 10^{-5}$  (Richter *et al.* 1999), but natural isotopic fractionation can vary this value by at least 0.5 – 14 times, therefore  $^{234}\text{U}$  is not a reliable indicator of anthropogenic contamination (Fleischer 2008). A ‘typical’ range for natural soils is given in (Szabo and Rosholt (1982), of 0.7 – 1.2. Therefore, isolated  $^{234}\text{U}/^{238}\text{U}$  measurements of environmental samples with less than 58 % DU contamination of total U cannot be resolved from natural.

### 5.2. Estimation of background uranium concentration

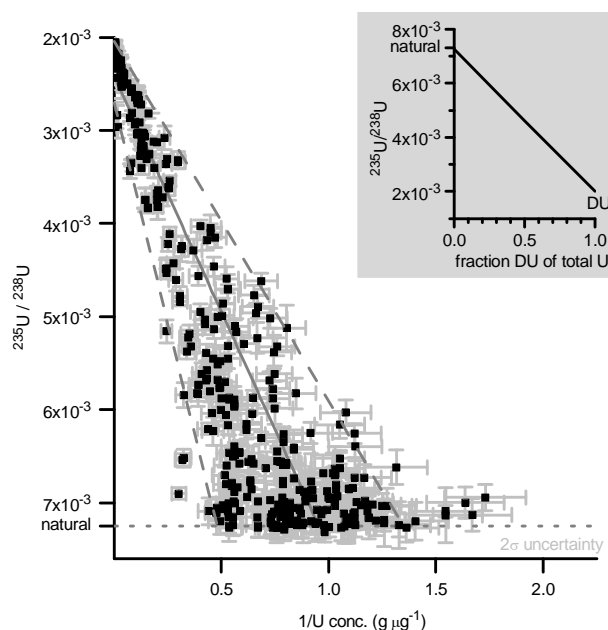
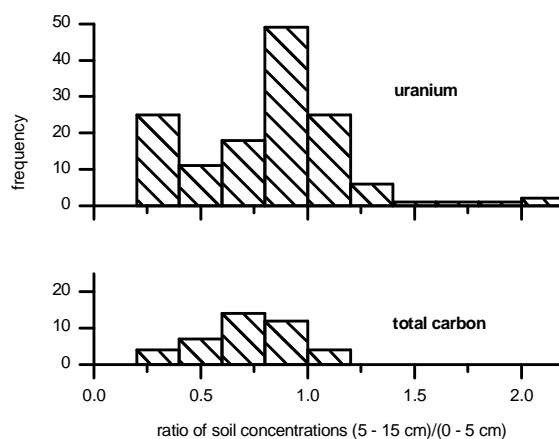


Figure 6. Plot of  $^{235}\text{U}/^{238}\text{U}$  against  $1/\text{uranium concentration}$  (all soils samples), which allows the natural background concentration range to be estimated for Colonie soils: weighted geometric mean  $1.05 \pm 0.06 \mu\text{g g}^{-1}$ ; range  $0.7 - 2.1 \mu\text{g g}^{-1}$  ( $n = 356$ ). Inset plot of  $^{235}\text{U}/^{238}\text{U}$  against the fraction DU of total U (after Bleise *et al.* 2003).

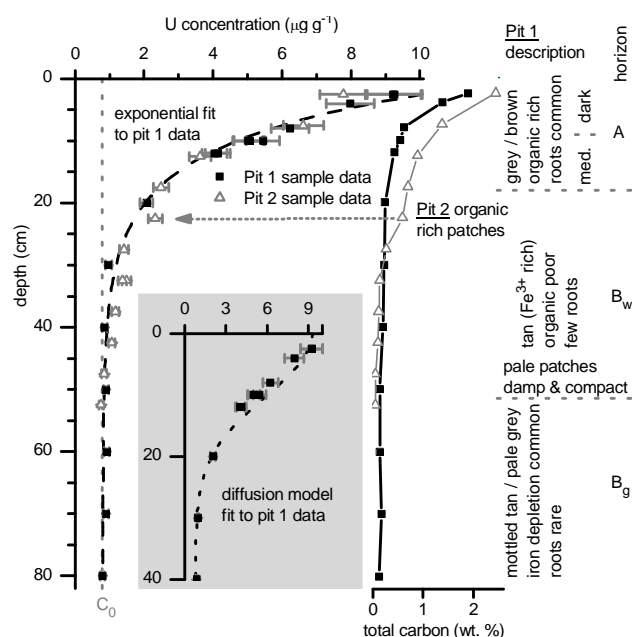
From the uranium concentration and isotope ratio data from the analysed samples, it is possible to estimate the range of natural uranium in the Colonie soils. Figure 6 shows that the concentration data spread out as the isotopic composition of natural uranium is approached. The concentration range for natural uranium can be estimated:  $0.7 - 2.1 \mu\text{g g}^{-1}$  with a weighted geometric mean of  $1.05 \pm 0.06 \mu\text{g g}^{-1}$ . This is significantly lower than  $6 \mu\text{g g}^{-1}$  estimated for this area by Jeter and Eagleson (1980), but slightly higher than the mean sediment concentration of  $0.6 \mu\text{g g}^{-1}$  for this area (USGS 2004).

### 5.3. Depth profiles



**Figure 7.** Histogram of the ratios of soil concentrations from two depth intervals, 5 – 15 and 0 – 5 cm from surface. Uranium concentration typically decreases from surface (median ratio 0.9). Total carbon ( $\approx$  organic carbon) also decreases from surface (median ratio 0.7).

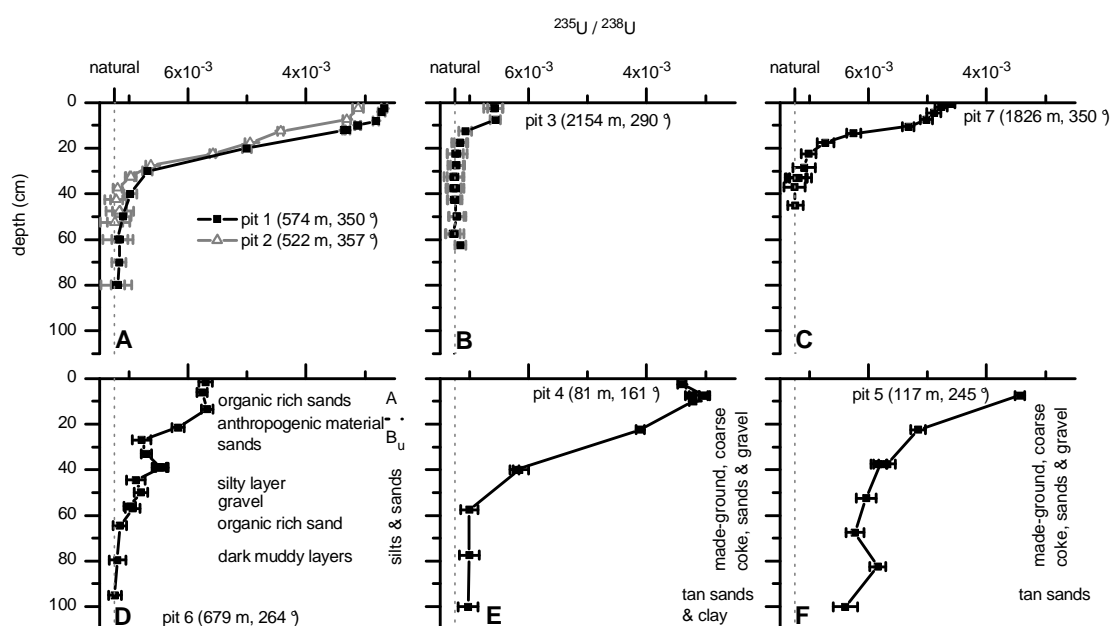
Figure 7 shows that there is typically a decrease in uranium concentration from the surface 0 – 5 cm interval to the 5 – 15 cm. There is also a decrease in total carbon from surface. These trends are explored in the following depth profiles.



**Figure 8 (left).** Uranium concentration against depth, showing similar trends from two adjacent sampling pits. An exponential line provides a good (weighted) fit to the concentration data from pit 1 (concentration =  $0.8 + 12.4 \times e^{-0.116 \times \text{depth}}$ , adj.  $R^2$  0.97). Inset, a simplistic diffusion model with coefficient ( $D$ ) of  $1.4 \text{ cm}^2 \text{ a}^{-1}$  approximates the pit 1 data.

**Figure 8 (right).** Total carbon (symbol size  $\approx$  uncertainty) also follows an exponential trend, decreasing with depth. Soil horizon description for pit 1; Stafford Series, somewhat poorly drained loamy fine sands, with negligible calcium carbonate content (USDA 2006). The water table was c. 1 m below surface in July and the mean soil pH was 4.8.

The concentrations from two depth profiles (c. 0.52 and 0.57 km N of NLI) are plotted in Figure 8. The two profiles follow a similar trend, and show an exponential decrease in concentration from surface, levelling off to a background concentration of c.  $0.8 \mu\text{g g}^{-1}$  beyond approximately 40 cm depth. Contamination decreases exponentially with depth in each of seven profiles, from pits of varying distance and direction from NLI, which are plotted for  $^{235}\text{U}/^{238}\text{U}$  in Figure 9.



**Figure 9.** Uranium isotope ratios with respect to soil depth, showing exponential increase from depleted values near surface to natural at depth, i.e. decrease in DU contamination. The dotted line is the natural isotopic composition. Labels state distance and bearing of sampling location from NLI.

Profiles in A – C are from woodland locations, with loamy fine sands similar to those previously described. The profile in D appears have been disturbed (proximal to I90); there is an apparent accumulation of DU contamination above a silty layer at 41 cm depth, beneath this fluvial sediments. E & F are from made-ground (sampled by hand auger, cross-contamination may account for the bump in F): the surface 90 cm comprises coke, sand and clay, beneath this are sands  $\pm$  clay; contamination persists to depths greater than 1.1 m.

Integration of the fitted exponential curve can be used to estimate the total deposition at this location, approximately  $0.9 \pm 0.2 \text{ g m}^{-2}$ . It is estimated that presently c. 45 % of the contamination is within the surface 5.1 cm (1979 survey interval), 82 % within the surface 15 cm (this study), and 99 % within 40 cm. It is therefore probable that the total mass of depleted uranium contamination was underestimated. However, the vertical distribution of contamination has probably changed since 1979.



Short-term soil mixing is discussed in Kaste *et al.* (2007), and dispersion of contaminants can be modelled by combinations of advection and diffusion and/or decomposition of the organic horizon. The advection term is from the downward flux of water through the soil surface, entraining dissolved, complexed and colloidal bound contaminant. An advection model would feature a pulse that had migrated downward from surface. Diffusion transport appears to control the observed uranium concentration depth profiles.

Bioturbation by deep burrowing (anecic) earthworms can be a significant mechanism for vertical transport of low-solubility and strongly sorbing contamination (Müller-Lemans & Van Dorp 1996), vertical burrows were observed in some of these soil profiles (Figure 4, Appendix 3). Earthworms are also known to be tolerant of heavy metal contamination (e.g. Sizmur & Hodson 2009), with a predicted no-effect concentration of at least  $100 \mu\text{g g}^{-1}$  for uranium (Sheppard *et al.* 2005).

Total carbon also decreases exponentially from surface, note the slight bump for pit 2 at 20 – 25 cm where organic rich patches were observed (heterogeneity); there is also a bump in the uranium curve. Oliver *et al.* (2008) observed similar trends for uranium and loss on ignition from firing range soils, but concluded that there was no significance for a direct relationship from their data. Differences in these exponential rates could be accounted for by the decomposition of organic material. It is possible that particulate is being physically mixed with organic carbon, or that dissolved uranium species are binding with the organic carbon.

Within the pH range of Colonie soils, in oxidising near-surface waters, either solid schoepite (hydrated uranyl oxy-hydroxide) or dissolved uranyl ( $\text{UO}_2^{2+}(\text{aq})$ ) are likely to be thermodynamically stable (Langmuir 1997). However, the Colonie soils are generally well-drained, and at least for oxidation in air, kinetics and surface passivation may limit bulk oxidation beyond  $\text{UO}_{2+x}(\text{s})$  (McEachern & Taylor 1998), as appears to be the case for a few primary particles recovered from Colonie soils (Chapter 3 / Lloyd *et al.* 2009b). Schoepite has a solubility three orders of magnitude greater than  $\text{UO}_{2+x}$  (Ragnarsdottir & Charlet 2000), therefore speciation is significant for contaminant transport and bioaccessibility.

The majority of uranyl ions from the oxidative dissolution of  $\text{UO}_2$  will strongly adsorb to ferric oxyhydroxides and organic matter in soils (Langmuir 1997); uranyl ions are rapidly removed from solution by association with organic matter (Dong *et al.* 2006). Sequential extraction of firing range soils shows an association of DU with the oxidisable ‘organic’ fraction (Oliver *et al.* 2008). However, it is not clear from the literature which extraction step would leach uranium oxide particulates or other uranium species. For both primary particulate (observed) and adsorbed uranyl species (expected), the contamination is likely to be dispersed by physical mixing.

The source term for the Colonie contamination is emissions of uranium oxide particulate into the atmosphere, settling by wet and dry deposition onto the soil surface from 1958 - 1984: a broad pulse input of slightly shorter duration than has occurred since emissions ceased (emissions records are not available). Most of the NLI feedstock appears to have been sourced from Paducah gaseous diffusion plant tails from 1967 – 1969 (Chapter 6 / Lloyd *et al. unpublished*), and most of the contamination from NLI appears to be from prior to 1979. Therefore, the period of significant input can be narrowed to 1967 – 1979.

A crude approximation of the source term is an instantaneous plane of DU on the soil surface 35 years before sampling. Contaminant concentration can then be modelled as a function of depth and time using the following diffusion equation from Crank (1975).

$$C = \frac{M}{\sqrt{\pi Dt}} e^{-\frac{z^2}{4Dt}}$$

Where **C** is the concentration of contaminant as a function of **z**, soil depth (cm), and **t**, time (years, a), **M** is the total mass of contaminant ( $\mu\text{g}$ ) estimated by integrating the present concentration profile. The coefficient of diffusion, **D** ( $\text{cm}^2 \text{a}^{-1}$ ) can be estimated by least squares fitting to the sample data.

For pit 1, a diffusion coefficient (**D**) of c.  $1.4 \text{ cm}^2 \text{a}^{-1}$  is estimated, and if maintained, the surface soil concentration will halve in approximately 125 years time (pedological half-life). The estimate for the adjacent pit, pit 2, is  $2.1 \text{ cm}^2 \text{a}^{-1}$ , giving a sense of the uncertainty involved. For a distant pit, pit 7, with approximately  $0.07 \pm 0.05 \text{ g m}^{-2}$  total contamination (**M**),  $1.4 \text{ cm}^2 \text{a}^{-1}$  was estimated. From these models, the proportion of contamination beneath 5.1 cm in 1979 was approximately one third (27 – 38 %), so it is likely that total contamination was c. 50 % greater than previously estimated, i.e. c. 4.8 tonnes<sup>2</sup>. This simplified model does not reflect deposition of contamination on these soils over a period.

The diffusion coefficients are of a similar magnitude to that measured using  $^{210}\text{Pb}$  for a bioturbated temperate mineral soil by Kaste *et al.* (2007). A similar approach could help refine the model of the Colonie contamination. They are also within the range reported by Bunzl (2002) and Schuller *et al.* (1997). The mixing time derived for the A horizon of pit 1 is approximately 222 years, equating to a mass turnover of c.  $0.6 \text{ kg m}^2 \text{a}^{-1}$ , compatible with earthworm bioturbation rates from temperate grasslands (summarised data in Bunnenberg & Taeschner 2000). Physical mixing by earthworms (bioturbation) can account for the redistribution of contamination and organic carbon within the A horizon, and the contaminant appears to have very limited mobility. It is likely that bioturbation by earthworms is dispersing contaminant from the soil surface, in the form of primary uranium oxide particulates and uranyl species that are adsorbed to organic matter.

Profiles E & F (Figure 9) are from made-ground situated between NLI and the railway. In 2006, these coarse, friable, coke-rich ‘soils’ (c. 25 - 50 wt. % loss on ignition) comprised uranium up to  $500 \pm 40 \mu\text{g g}^{-1}$  (for Pb  $1180 \pm 142$ , Cu  $1386 \pm 166$ , Sn  $279 \pm 34$ , Sb  $27 \pm 3 \mu\text{g g}^{-1}$ ). Subsequently this area was remediated by replacing some of the surface material with clean fill. These profiles were sampled by hand auger in 2007 (pit sampling was not possible). The top of profile E reflects replacement of the surface with cleaner material. Profiles E & F show an exponential increase in  $^{235}\text{U}/^{238}\text{U}$ , but they do not reach natural composition within the surface 1.1 m.

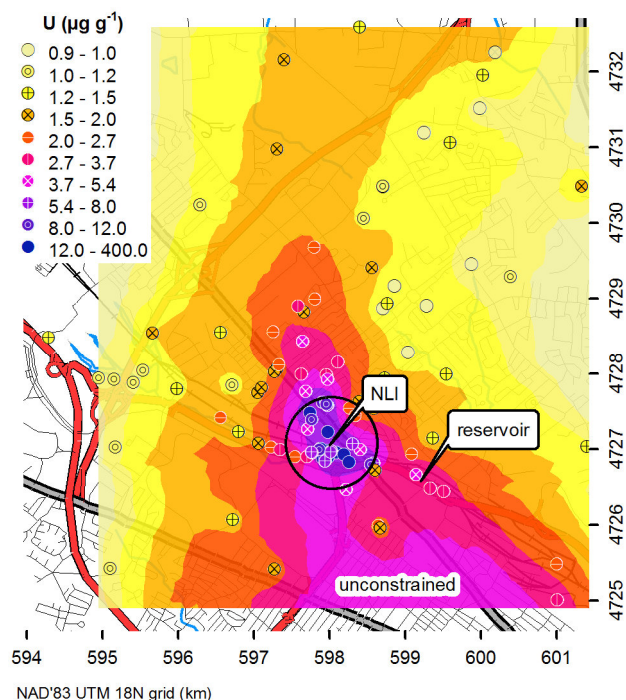
#### 5.4. Uranium contamination map (concentration)

The concentration data from shallow soils are plotted and interpolated in Figure 10. Uranium concentrations greater than  $12 \mu\text{g g}^{-1}$  were excluded from the interpolation, because these heavily skew the dataset. The excluded data were mostly within 200 m of NLI and access to undisturbed sites within the north of this area was difficult. This dataset does not significantly increase the estimate of total uranium emissions, which are concentrated within the area of the 1979 survey. Significantly elevated concentrations ( $3.4 \pm 0.3 \mu\text{g g}^{-1}$ ) are measured up to 1.9 km NNW of NLI, likely to comprise 31 – 81 % contamination of total uranium.

The concentration of  $^{238}\text{U}$  (converted from activity) for surface soils on the railroad south of NLI in 1968 were reported as  $163 \mu\text{g g}^{-1}$  (NYSDOH 1979), in 1979 up to  $3080 \pm 65$  (Jeter & Eagleson

<sup>2</sup> The uncertainty on this figure was estimated to be in the order of  $\pm 1$  tonne.

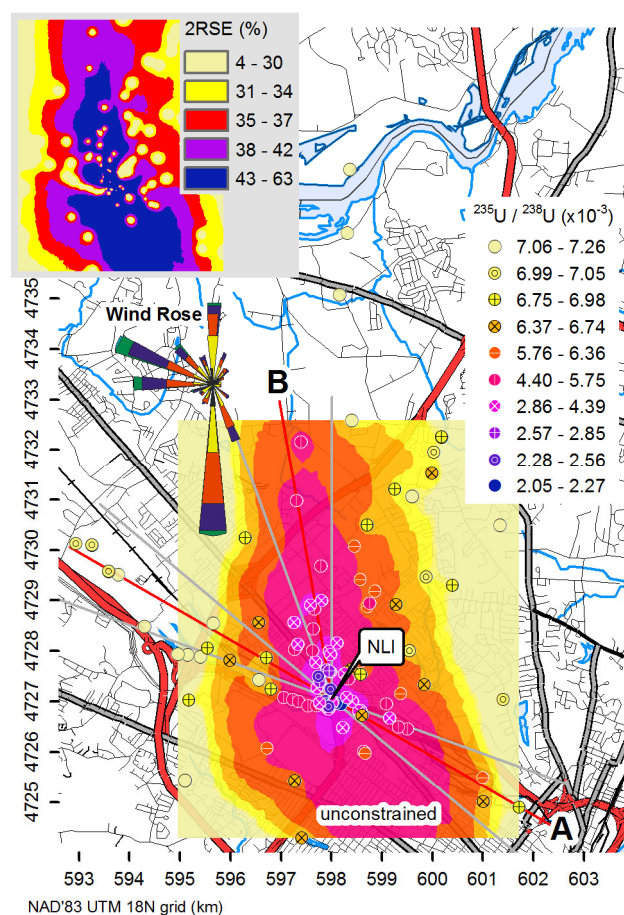
1980). The representativity and comparability of the earlier measurement is not clear, but it suggests that the majority of the contaminant uranium probably occurred during 1968-1979. Proximal locations, within 30 m of each other, comprised  $458 \pm 16 \mu\text{g g}^{-1}$  in 1979,  $500 \pm 40 \mu\text{g g}^{-1}$  in 2006, and then after environmental remediation in 2007,  $7.9 \pm 0.6 \mu\text{g g}^{-1}$ .



**Figure 10.** Map of uranium concentration in surface soils (0 - 5 cm), ordinary kriging excluding data greater than  $12 \mu\text{g g}^{-1}$  (log transform, quadratic trend removal, exponential semivariogram model; cross-validation statistics: mean standardised error 0.03,  $\text{RM}^2$  standardised error 0.97). The southern extent is poorly constrained, due to difficulty accessing undisturbed sites in this more densely populated neighbourhood; Figure 2 (1979 survey extent circled) suggests that the southward distribution is much less extensive than shown here. A sediment core from the labelled reservoir was previously analysed by Arnason and Fletcher (2003).

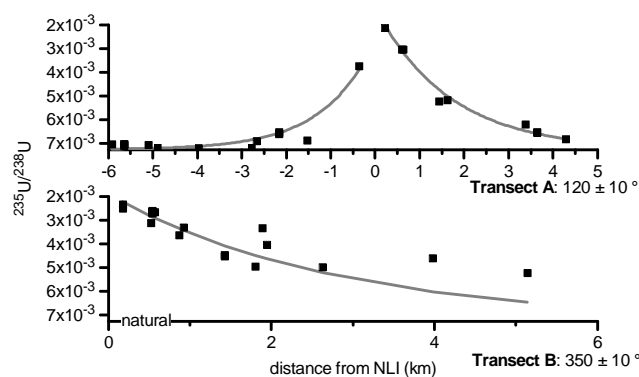
A sediment core from the Patroon reservoir (labelled) was sampled and analysed by Arnason and Fletcher (2003), with mean and maximum uranium concentrations of  $13$  and  $320 \mu\text{g g}^{-1}$ . In contrast, the surface soil concentration interpolated for this location is  $3.6 \pm 2.9 \mu\text{g g}^{-1}$ . This clearly shows that uranium accumulated in the reservoir sediment, either from runoff from the Patroon creek watershed, or from direct discharges from the NLI site into the Patroon Creek (approximately 1.6 km upstream). Some of the reservoir sediment contaminant appears to be from  $\text{U(VI)}$  species (Arnason *et al.* 2008), implying at least some dissolution and reprecipitation.

### 5.5. DU contamination map (isotope ratio)



**Figure 11.** Map showing the distribution of DU contamination in surface soils (0 – 5 cm) using ordinary kriging (quadratic trend removal, exponential semivariogram model; cross validation statistics: mean standardised error - 0.0073,  $RM^2$  standardised error 0.95, relative standard error map inset). The southern extent is poorly constrained, due to difficulty accessing undisturbed sites in this densely populated neighbourhood; Figure 2 suggests that the southward distribution is much less extensive than shown here. DU has been detected in soils at least 5.1 km NNW of NLI (DU detection limit c.  $7.06 \times 10^{-3} {}^{235}\text{U}/{}^{238}\text{U}$ ). Wind rose from Figure 2, approximate weather station location. Transect lines marked A and B are referred to in Figure 12.

A map of  ${}^{235}\text{U}/{}^{238}\text{U}$  is presented in Figure 11, which reveals the extent of DU contamination. The previously discussed surface sample, 1.9 km NNW of NLI comprises  $(3.34 \pm 0.06) \times 10^{-3} {}^{235}\text{U}/{}^{238}\text{U}$ , 73 – 76 % DU of total U (see Figure 6 inset). More than one third of the total uranium in a surface soil sample from 5.1 km NNW of NLI is depleted uranium contamination. These maps demonstrate the sensitivity and potential precision of  ${}^{235}\text{U}/{}^{238}\text{U}$  for defining the contamination footprint. This approach could be used to assess the historic exposure potential of residents, a prerequisite for a proposed health study in the Colonie area. Exposure of a sub-group could be verified using urine analyses (Parrish *et al.* 2008).



**Figure 12.** Profiles drawn along transects A and B (marked on Figure 11), from measured data (symbol height  $\approx$  uncertainty), showing an exponential increase in  $^{235}\text{U}/^{238}\text{U}$  towards natural with increasing distance from NLI. Equations: Transect A (NW)  $y = 7.253 \times 10^{-3} - 4.6 \times 10^{-3} e^{-0.0009x}$ , adj.  $R^2$  0.90; Transect A (SE)  $y = 7.253 \times 10^{-3} - 6.0 \times 10^{-3} e^{-0.0006x}$ , adj.  $R^2$  0.99; Transect B:  $y = 7.253 \times 10^{-3} - 5.3 \times 10^{-3} e^{-0.0003x}$ , adj.  $R^2$  0.75. Differences in the exponential rates can be attributed to wind speed frequency distributions for each direction (see Figure 11 for wind rose).

Figure 12 plots sample data from two transects crossing NLI (as marked on Figure 11). Transect B roughly follows the primary axis of deposition, transect A is at a divergent angle to this. The isotope ratios increase towards natural with distance from NLI, following exponential trends. This is typical of point-source atmospheric pollutant dispersal (e.g. De Caritat *et al.* 1997). The differences in exponential rate can be attributed to differences in wind speed frequency distributions for each direction; winds blowing towards  $350 \pm 5^\circ$  occurred 6.4 % of the time, towards  $120 \pm 5^\circ$  for 4.5 % of the time,  $300 \pm 5^\circ$  for 5.1 % but at lower speeds.

The typical detection limit for DU of  $7.06 \times 10^{-3} \text{ }^{235}\text{U}/^{238}\text{U}$  is equivalent to 4 % DU of total U,  $0.05 \mu\text{g g}^{-1}$  DU with  $1 \mu\text{g g}^{-1}$  NU, or one 84  $\mu\text{m}$  diameter DU dioxide particle in a 60 g aliquot of typical Colonie soil. Therefore, there could be potential for nugget effect during sub-sampling prior to milling. However, the aerodynamic diameter of such a particle is large, and dry deposition is likely within 100 m of NLI (if initially convected to 20 m above surface and transported by a high wind at  $11 \text{ m s}^{-1}$ ) where surface soil DU concentrations are much higher.

DU contamination has been detected to at least 5.6 km WNW of NLI (against prevailing wind),  $(7.03 \pm 0.04) \times 10^{-3} \text{ }^{235}\text{U}/^{238}\text{U}$  ( $n = 4$ ). Approximately 42 ng of DU contaminates each gram of soil, equivalent to approximately 45 DU dioxide particles of 6  $\mu\text{m}$  diameter (plausible for air transport at a more usual  $3 \text{ m s}^{-1}$ ) are required to ‘contaminate’ each gram of sample. Winds favourable for transport to that location were rare, occurring only 0.5 % of the time. This area of the Pine Bush Preserve had recently been affected by a fire, and it is possible that this concentrated contamination from the combusted vegetation onto the soil surface.

## 6. Conclusions

The Colonie case-study has been suggested as a reasonable analogue for battlefield contamination by depleted uranium. In this paper, uranium isotope ratios measured by ICP-QMS have revealed the extent and spatial distribution of DU contamination surrounding the former NLI site. The mass of DU contamination surrounding NLI, within the surface 5.1 cm soils in 1979 was

approximately 3.2 tonnes, but the total may be closer to 4.8 tonnes. This is significant within the context of emissions from battlefield deployment of DU munitions.

The quality control data show that accurate isotope ratios can be reliably measured by ICP-QMS without the need for costly separation chemistry. Multi-isotope ratio plots resolve heterogeneity of the DU compositions previously observed from individual particle analyses. There is no evidence of enriched uranium in the bulk soil samples.

DU contamination can be detected in surface soils to at least 5.6 km from the NLI site using  $^{235}\text{U}/^{238}\text{U}$ . With further sampling and analyses, the northward contamination plume could be mapped in detail using this method. This would be useful for constraining the historic exposure potential of residents for proposed health studies in the Colonie area.

Isotope ratio and concentration data allow the natural background range of uranium concentration in Colonie soils to be estimated,  $0.7 - 2.1 \mu\text{g g}^{-1}$  with a weighted geometric mean of  $1.05 \pm 0.06 \mu\text{g g}^{-1}$ . The areal distribution of contamination was clearly controlled by prevailing winds.

The vertical distribution of DU contamination is closely related to the carbon content in the surface soil horizon, and can be explained by diffusion-like physical mixing. It is likely that bioturbation by earthworms is dispersing this low mobility contaminant from the soil surface, in the form of primary uranium oxide particulates and uranyl species that are adsorbed to organic matter.

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